If, as Natta and coworkers[4,12] believe, isotactic polymerization proceeds from catalytic sites each of which preferentially generates asymmetric centers of one kind, *d* or *l*, then the residual racemic dyads must occur in pairs $\cdots mrrm \cdots$ in a predominantly isotactic chain.[1,14] The racemic resonances are then divided equally between *rrm;* 1 and *rrm;* 2, in the notation of Table I. One of these occurs upfield and the other downfield from the frequency characteristic of the racemic dyad in a syndiotactic polymer. Both will be broadened, and shifted as well, compared to the resonance for the predominantly syndiotactic polymer. Since the resonances for the racemic dyad are divided between two peaks, the limits of detection must be correspondingly raised.

In conclusion, the detailed analyses of chain conformation in relation to stereochemical configurations presented in this paper, together with the confirmatory nmr results of Zambelli and Segre,[8] show beyond reasonable doubt that small proportions of racemic dyads in predominantly isotactic chains of vinyl polymers such as polypropylene may easily escape detection by nmr spectroscopy. High degrees of stereoregularity should not be inferred from the absence of detectable resonances attributable to racemic dyads.

(14) This mechanism is implausible for atactic polymers for which $f_r \approx 0.5$.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Contract No. AF 49(638) 1341.

Preferential Orientation and Strain–Dichroism of Polymer Chains

P. J. Flory and Y. Abe

Department of Chemistry, Stanford University, Stanford, California 94305.
Received May 14, 1969

ABSTRACT: A general theory of dichroism induced by strain in polymeric networks is developed by adaptation of methods recently published for treating strain birefringence. It is generally applicable to dichroic bands associated with any specified conformation involving sequences of one or more consecutive bonds. The transition dipole moment is introduced in the local framework of the skeletal bonds associated therewith. Possible differences in transition moments for various conformations and repeat units are taken into account without difficulty. Numerical calculations for polymethylene chains show *gauche* (*g*) bonds, rather than *trans* (*t*), to be more favorably oriented with respect to the chain vector **r**. The *g* bond in the *tgt* conformation for three consecutive bonds undergoes a comparatively high orientation; the *t* bond in *gtg* is preferentially oriented transverse to **r**. Orientations of other symmetry axes for various conformations are calculated, and the results are found to be in qualitative accord with the dichroic ratios observed for amorphous polyethylene by Read and Stein.

Dichroism induced by strain in polymers reflects preferential orientation of the transition dipole moment for absorption of radiation of given frequency. The transition moments for various absorption processes differ in their orientations with respect to the chain skeleton, and a given absorption may be contingent upon the occurrence of a specific backbone conformation. It is not surprising, therefore, that the strain-induced orientations indicated by dichroic measurements at various frequencies differ markedly, as Read and Stein[1] have shown. The sign and magnitude of the orientation indicated by the dichroic ratio may be expected to depend on the direction of the transition dipole with respect to the local bond structure and conformation. Elucidation of the relationship requires a detailed accounting of the configurational statistics of the chain as a whole.

Methods[2-4] developed for the treatment of strain birefringence can be adapted to the interpretation of strain–dichroism, as one of us has pointed out.[4] Both depend on quantities which can be expressed as second-order tensors. Rigorous treatment of strain–dichroism on this basis is presented here. Calculations carried out for various absorptions in the infrared spectrum of polymethylene chains are included as well. The results of these calculations are illustrative of the connection between preferential orientation of a transition moment and (a) its specification within a reference frame affixed to the local structure, and (b) the skeletal conformation required for occurrence of the absorption process.

(1) B. E. Read and R. S. Stein, *Macromolecules*, **1**, 116 (1968).
(2) K. Nagai, *J. Chem. Phys.*, **40**, 2818 (1964); **47**, 2052 (1967).
(3) P. J. Flory, R. L. Jernigan, and A. E. Tonelli, *ibid.*, **48**, 3822 (1968).
(4) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., Chapter IX.

Theory

Let $\mathbf{m}_i$ be the transition moment for the absorption of electromagnetic radiation at a frequency ν by skeletal bond i, or by groups associated therewith. Further, let $\boldsymbol{\epsilon}_i$ be the dyadic representation of $\mathbf{m}_i\mathbf{m}_i$. Then the absorbance (and the extinction coefficient) for radiation with polarization vector parallel to $\mathbf{m}_i$ will be proportional to $\epsilon_i = \text{trace } \boldsymbol{\epsilon}_i = m_i^2$, where m_i is the scalar magnitude of $\mathbf{m}_i$. For random orientation of bond i with respect to the incident radiation, the absorbance will be proportional to $\bar{\epsilon}_i = \epsilon_i/3$.

The absorbance of the molecule as a whole may be formulated as the appropriate tensor sum over the $\boldsymbol{\epsilon}_i$ associated with the skeletal bonds comprising the chain. In the evaluation of this sum, account must be taken of differences in transition moments, as embodied in the $\boldsymbol{\epsilon}_i$, for various bonds or repeat units of the chain; for

some of them ϵ_i may be null, for example. The absorbance may depend moreover on the conformation of bond i, and perhaps on the conformations of neighboring bonds as well. The treatment which follows is designed to take account of all features of this nature peculiar to absorption at the specified frequency. Accordingly, the relative absorbance of plane polarized radiation by the molecule comprising n skeletal bonds is represented in dyadic, or tensor, form by

$$\boldsymbol{\epsilon} = \sum_{i=1}^{n} p_{\eta;i}\boldsymbol{\epsilon}_i \tag{1}$$

where $p_{\eta;i}$ is the *a priori* probability that bond i occurs in the rotational state η required for the absorption of frequency ν; or, if a sequence of several bonds, including bond i, must assume a certain conformation in order for absorption to occur, then η will denote this conformation, collectively, for bond i and its neighbors. The rotational state designation η will be understood to apply to $\boldsymbol{\epsilon}$ and to $\boldsymbol{\epsilon}_i$ as well; it is omitted as a subscript in the interest of simplifying the notation. Molecular quantities such as $\boldsymbol{\epsilon}$ are distinguished from the corresponding bond or group quantities (*i.e.*, $\boldsymbol{\epsilon}_i$) by the absence of a serial index subscript.

The molecular absorbance averaged over all orientations of the molecule is proportional to

$$\bar{\epsilon} = (1/3)\text{trace } \boldsymbol{\epsilon} = \sum p_{\eta;i}\bar{\epsilon}_i \tag{2}$$

Let ϵ_r be the mean absorbance for light with polarization vector parallel to the chain vector $\mathbf{r}$ (*i.e.*, the end-to-end vector) for a specified value r of the magnitude of $\mathbf{r}$; symbolically expressed

$$\epsilon_{\parallel r} = \epsilon_r \tag{3}$$

by definition. Since the array of configurations having the specified value of r is cylindrically symmetric about $\mathbf{r}$, the mean absorbance of radiation polarized perpendicular to $\mathbf{r}$ is

$$\epsilon_{\perp r} = (3\bar{\epsilon} - \epsilon_r)/2 \tag{4}$$

Pursuant to the evaluation of ϵ_r, we consider the average component $\epsilon_{r;i}$ of ϵ_i along the chain vector $\mathbf{r}$. Thus, if Φ_i is the angle between the transition moment and $\mathbf{r}$, then

$$\epsilon_{r;i}/\epsilon_i = \langle\cos^2\Phi_i\rangle_r \tag{5}$$

where the angle brackets denote the average taken over all configurations of the chain consistent with the specified value of r and the occurrence of bond i (and its neighbors) in the specified conformation η. Expanding this quantity in even powers of r, after the manner of the treatment of strain birefringence,[2-5] we have

$$\langle\cos^2\Phi_i\rangle_r = \frac{1}{3} + \beta_{2;i}\left(\frac{r^2}{\langle r^2\rangle_0}\right) + \beta_{4;i}\left(\frac{r^4}{\langle r^2\rangle_0^2}\right) + \cdots \tag{6}$$

where the subscript zero appended to angle brackets denotes the average over all configurations for the unperturbed chain free of constraints.

If considerations are limited to chains at low extensions, the series may be truncated at the term in r^2. We proceed on the premise that the expression thus abbreviated will suffice. The constant $\beta_{2;i}$ may then be evaluated through multiplication by r^2 and averaging over all configurations for the unconstrained chain with bond i in state η. The result obtained is[2-5]

$$\beta_{2;i} = \left(\frac{\langle r^2\rangle_0^2}{\langle r^4\rangle_0}\right)\left[\frac{\langle r^2\cos^2\Phi_i\rangle_0}{\langle r^2\rangle_0} - \frac{1}{3}\right] \tag{7}$$

or, since $\langle r^4\rangle_0/\langle r^2\rangle_0^2$ approaches 5/3 for long chains

$$\beta_{2;i} = (3/5)[(\langle r^2\cos^2\Phi_i\rangle_0/\langle r^2\rangle_0) - (1/3)] \tag{8}$$

and, according to eq 6, with higher terms omitted

$$\langle\cos^2\Phi_i\rangle_r - (1/3) = \beta_{2;i}(r^2/\langle r^2\rangle_0) \tag{9}$$

Thus, $\beta_{2;i}$ is the constant of proportionality (for small extensions) between the departure of $\langle\cos^2\Phi_i\rangle_r$ from its value of one-third for the free chain and the square of the extension represented by $r^2/\langle r^2\rangle_0$. According to eq 8, $\beta_{2;i}$ measures the correlation of the direction of the moment $\mathbf{m}_i$ with the direction of the chain vector $\mathbf{r}$; positive and negative values of $\beta_{2;i}$ denote preferences for parallel and transverse orientations, respectively.[6]

An equivalent definition of $\beta_{2;i}$ is

$$\beta_{2;i} = (3/5)\langle\mathbf{r}^{\mathrm{T}}\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0/\epsilon_i\langle r^2\rangle_0 \tag{10}$$

where $\mathbf{r}$ is expressed as a column vector, $\mathbf{r}^{\mathrm{T}}$ is its row form, and $\hat{\boldsymbol{\epsilon}}_i$ is the traceless tensor defined by

$$\hat{\boldsymbol{\epsilon}}_i = \boldsymbol{\epsilon}_i - \bar{\epsilon}_i\mathbf{E} \tag{11}$$

$\mathbf{E}$ being the identity matrix. Inasmuch as $\boldsymbol{\epsilon}_i/\epsilon_i$ is the dyadic formed from the unit vector along the transition moment $\mathbf{m}_i$, it will be apparent from eq 10 and 11 that $\beta_{2;i}$ represents the tendency of the transition moment $\mathbf{m}_i$ to correlate with vector $\mathbf{r}$. The optical absorption anisotropy for bond i is expressed by eq 8–11 in a form analogous to that developed previously for the optical polarizability and its connection with the strain birefringence.

For the chain molecule as a whole

$$\begin{aligned}\epsilon_r &= \sum_i p_{\eta;i}\epsilon_i\langle\cos^2\Phi_i\rangle_r \\ &= \bar{\epsilon} + (\sum_i p_{\eta;i}\epsilon_i\beta_{2;i})(r^2/\langle r^2\rangle_0)\end{aligned} \tag{12}$$

where $\bar{\epsilon}$ is average molecular absorbance defined by eq 2.

It follows that

$$\epsilon_r - \bar{\epsilon} = G_2(r^2/\langle r^2\rangle_0) \tag{13}$$

where[7]

(5) M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," S. N. Timasheff and M. J. Timasheff, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 7.

(6) As will be apparent from scrutiny of eq 8 and 10, $\beta_{2;i}$ is of order $1/n$; hence, as it stands, this quantity is unsuitable for characterizing the correlation of a transition moment within chains of given generic type. A more direct measure of the correlation would be afforded by the quantity $(3/5)\langle\mathbf{r}^{T}\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0/\epsilon_i l^2$, where the square of the bond length l^2 may be averaged over all skeletal bonds of the chain in the event that their lengths differ. Simplicity of exposition favors use of $\beta_{2;i}$ in the text. Moreover, its definition accords with the corresponding quantity introduced in the treatment of the strain birefringence.[3,4]

(7) The quantity G_2 corresponds to $(2/3)\Gamma_2$ where Γ_2 is its analog in the theory of strain birefringence.[3,4] If $\Delta\epsilon_r$ represents the difference between the components of $\boldsymbol{\epsilon}$ parallel and perpendicular, respectively, to $\mathbf{r}$, then according to eq 3, 4, and 13

$$\Delta\epsilon_r = (3/2)(\epsilon_r - \bar{\epsilon}) = (3/2)G_2(r^2/\langle r^2\rangle^0)$$

Since we shall not deal explicitly with $\Delta\epsilon_r$, the quantity G_2 is preferred here.

$$G_2 = \sum_i p_{\eta;i}\epsilon_i\beta_{2;i} \tag{14}$$

$$= (3/5)\sum_i p_{\eta;i}\langle \mathbf{r}^T\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0/\langle r^2\rangle_0 \tag{15}$$

If the *magnitude* of the absorbance is the same for all absorbing groups that occur in the required conformation η, *i.e.*, if $\epsilon_i = \epsilon_\eta$ for all i, then

$$G_2 = \epsilon_\eta\sum_i p_{\eta;i}\beta_{2;i}$$

$$= (3/5)\epsilon_\eta\sum_i p_{\eta;i}\langle \mathbf{r}^T(\hat{\boldsymbol{\epsilon}}_i/\epsilon_i)\mathbf{r}\rangle_0/\langle r^2\rangle_0 \tag{16}$$

Thus, G_2 expresses the *sum* of the correlations of the directions of the transition moments for all absorbing groups with the chain vector $\mathbf{r}$. It is asymptotic with the number of bonds n.

The relative absorbance of radiation with polarization vector parallel to the X axis of an arbitrary Cartesian reference frame, taken as the mean for all absorbing groups in the molecule, is

$$\epsilon_{xx} = \epsilon_{\parallel r}\cos^2(X, r) + \epsilon_{\perp r}\sin^2(X, r) \tag{17}$$

where (X, r) denotes the angle between X and $\mathbf{r}$. Letting x, y, and z denote the components of $\mathbf{r}$ in the chosen reference frame and substituting from eq 3 and 4, we have

$$\epsilon_{xx} - \bar{\epsilon} = (1/2)(\epsilon_r - \bar{\epsilon})(3x^2/r^2 - 1)$$

which in combination with eq 13 gives

$$\epsilon_{xx} - \bar{\epsilon} = (1/2)G_2\left(\frac{3x^2}{\langle r^2\rangle_0} - \frac{r^2}{\langle r^2\rangle_0}\right) \tag{18}$$

Corresponding expressions hold for ϵ_{yy} and ϵ_{zz}.

The absorbances for a network subject to a homogeneous deformation follow directly from eq 18 through replacement of x^2 by its mean value $\overline{x^2}$ for all chains of the network.[4] If the strain is specified by principal extension ratios λ_x, λ_y, and λ_z defined relative to a reference state such that $\overline{x^2} = \overline{y^2} = \overline{z^2} = \langle r^2\rangle_0/3$, then $\lambda_x^2 = 3\overline{x^2}/\langle r^2\rangle_0$, etc. Hence, for the strained network

$$\epsilon_{xx} - \bar{\epsilon} = (G_2/3)[\lambda_x^2 - (\lambda_y^2 + \lambda_z^2)/2] \tag{19}$$

where ϵ_{xx} and $\bar{\epsilon}$ represent mean absorbances defined as above. Corresponding expressions hold for ϵ_{yy} and ϵ_{zz}. Hence

$$\epsilon_{xx} - \epsilon_{yy} = (G_2/2)(\lambda_x^2 - \lambda_y^2) \tag{20}$$

For simple elongation, with X as the longitudinal axis, we let

$$\lambda_x^2 = (V/V_0)^{2/3}\alpha^2$$

where V is the volume in the state of strain, V_0 is the volume in the reference state, and $\alpha \equiv \alpha_x$ is the length of the elongated specimen relative to its relaxed (isotropic) length at the *same volume* V. Thus (V/V_0) measures the volume dilation, and α the distortion at *fixed volume* V. It follows that $\lambda_y^2 = \lambda_z^2 = (V/V_0)^{2/3}/\alpha$. Making these substitutions in eq 19, we have

$$\epsilon_{xx} = \bar{\epsilon} + (G_2/3)(V/V_0)^{2/3}(\alpha^2 - 1/\alpha) \tag{21}$$

and

$$\epsilon_{yy} = \epsilon_{zz} = \bar{\epsilon} - (G_2/6)(V/V_0)^{2/3}(\alpha^2 - 1/\alpha) \tag{22}$$

The departure of the dichroic ratio, $D = \epsilon_{xx}/\epsilon_{yy}$, from unity is given by

$$D - 1 = \frac{(G_2/2)(V/V_0)^{2/3}(\alpha^2 - 1/\alpha)}{\bar{\epsilon} - (G_2/6)(V/V_0)^{2/3}(\alpha^2 - 1/\alpha)} \tag{23}$$

$$\approx (G_2/2\bar{\epsilon})(V/V_0)^{2/3}(\alpha^2 - 1/\alpha) \tag{24}$$

or[4,5]

$$D - 1 \approx (G_2/2\bar{\epsilon}\nu kT)t_\alpha \tag{25}$$

where t_α is the stress exhibited by the network of ν chains at extension ratio α and volume V.

The quantities $\beta_{2;i}$ and G_2, essential for treating the strain dichroism of various transitions, may be deduced by application of methods detailed elsewhere. To this end let matrices be defined as[3,4]

$$\mathbf{A}_i = \begin{bmatrix} \mathbf{U} & (\mathbf{U}\times\mathbf{l}^T)_{\|}\mathbf{T}_{\|} & (1/2)(\mathbf{U}\times\mathbf{l}^T\times\mathbf{l}^T)_{\|}\mathbf{T}\times\mathbf{T}_{\|} \\ \mathbf{0} & (\mathbf{U}\times\mathbf{E}_3)_{\|}\mathbf{T}_{\|} & (\mathbf{U}\times\mathbf{E}_3\times\mathbf{l}^T)_{\|}\mathbf{T}\times\mathbf{T}_{\|} \\ \mathbf{0} & \mathbf{0} & (\mathbf{U}\times\mathbf{E}_9)_{\|}\mathbf{T}\times\mathbf{T}_{\|} \end{bmatrix}_i \tag{26}$$

$$\mathbf{B}_i = \begin{bmatrix} (\mathbf{U}\times\hat{\boldsymbol{\epsilon}}^R)_{\|}\mathbf{T}\times\mathbf{T}_{\|} & \mathbf{U}\times[\hat{\boldsymbol{\epsilon}}^R(\mathbf{l}\times\mathbf{E}_3)]_{\|}\mathbf{T}_{\|} & (1/2)\mathbf{U}[\hat{\boldsymbol{\epsilon}}^R(\mathbf{l}\times\mathbf{l})] \\ \mathbf{0} & (\mathbf{U}\times\hat{\boldsymbol{\epsilon}})_{\|}\mathbf{T}_{\|} & \mathbf{U}\times[(\mathbf{E}_3\times\mathbf{l}^T)\hat{\boldsymbol{\epsilon}}^C] \\ \mathbf{0} & \mathbf{0} & \mathbf{U}\times\hat{\boldsymbol{\epsilon}}^C \end{bmatrix}_i \tag{27}$$

$$\mathbf{C}_i = \begin{bmatrix} (\mathbf{U}\times\mathbf{E}_9)_{\|}\mathbf{T}\times\mathbf{T}_{\|} & (\mathbf{U}\times\mathbf{l}\times\mathbf{E}_3)_{\|}\mathbf{T}_{\|} & (1/2)(\mathbf{U}\times\mathbf{l}\times\mathbf{l}) \\ \mathbf{0} & (\mathbf{U}\times\mathbf{E}_3)_{\|}\mathbf{T}_{\|} & \mathbf{U}\times\mathbf{l} \\ \mathbf{0} & \mathbf{0} & \mathbf{U} \end{bmatrix}_i \tag{28}$$

where subscripts i external to brackets apply to the various unsubscripted quantities within. The statistical weight matrix for bond i is represented by $\mathbf{U}_i$, and the transformation from the coordinate system of bond $i+1$ to that for bond i by $\mathbf{T}_i$; $_{\|}\mathbf{T}_{i\,\|}$ denotes the diagonal array of matrices $\mathbf{T}_i^\eta$, $\mathbf{T}_i^\zeta$, etc., for the various rotational states ζ, η, etc, about bond i; $_{\|}\mathbf{T}_i\times\mathbf{T}_{i\,\|}$ similarly denotes the diagonal array of the indicated direct products $\mathbf{T}_i^\eta\times\mathbf{T}_i^\eta$ etc.; the bond vector $\mathbf{l}_i$ is expressed as the column of its elements, l_i, 0, 0, in its own reference frame, and $\mathbf{l}_i^T$ is the transpose thereof; $\mathbf{E}_3$ and $\mathbf{E}_9$ are the identity matrices of the orders indicated by subscript; $\hat{\boldsymbol{\epsilon}}_i^R$ is the row comprising the elements of $\hat{\boldsymbol{\epsilon}}_i$, arranged in the following order

$$\hat{\boldsymbol{\epsilon}}_i^R = [\hat{\epsilon}_{i11}, \hat{\epsilon}_{i12}, \hat{\epsilon}_{i13}, \hat{\epsilon}_{i21}, \ldots \hat{\epsilon}_{i33}]_i$$

with $\hat{\boldsymbol{\epsilon}}_i$ expressed in the reference frame of bond i; $\hat{\boldsymbol{\epsilon}}_i^C$ is the corresponding column. Direct matrix products are denoted by $\times$ throughout this paper.

If the absorbance associated with skeletal bond i is independent of the conformation, then according to methods developed for treating various average properties of chain molecules,[3,4] we have

$$\langle \mathbf{r}^T\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0 = 2\mathcal{J}^*\mathbf{A}_1^{(i-1)}\mathbf{B}_i\mathbf{C}_{i+1}^{(n-i-1)}\mathcal{J}/Z \tag{29}$$

where $\mathcal{J}^*$ is the row of elements 1, 0, 0, . . . 0, and $\mathcal{J}$ is the column of elements 0, 0, . . . 0, 1, 1, 1; $\mathbf{A}_1^{(i)}$ is the

serial product comprising i factors commencing with $\mathbf{A}_1$ and $\mathbf{C}_{i+1}{}^{(n-i-1)}$ is the serial product correspondingly defined by its suffixes; Z is the partition function calculated from the same statistical weight matrices $\mathbf{U}$ entering into $\mathbf{A}_i$, $\mathbf{B}_i$, and $\mathbf{C}_i$. Substitution of this result into eq 10, together with $\langle r^2\rangle_0$ calculated by methods given previously, leads to $\beta_{2;i}$.

In cases of main interest the absorption associated with bond i occurs only when this bond assumes the particular conformation which we designate by η. (Cases in which a sequence of two or more bonds are required to occur in a specified conformation are separately treated below.) In this situation, the required quantity is given by

$$\langle \mathbf{r}^{\mathrm{T}}\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0 = 2\mathcal{J}^*\mathbf{A}_1{}^{(i-1)}\mathbf{B}_{\eta;i}'\mathbf{C}_{i+1}{}^{(n-i-1)}\mathcal{J}/Z_{(\eta,i)}' \quad (30)$$

where $\mathbf{B}_{\eta;i}'$ is the matrix formed from $\mathbf{B}_i$ by making all columns of $\mathbf{U}_i$ null with the exception of column η which is retained intact; $Z_{(\eta,i)}'$ is the partition function calculated with $\mathbf{U}_i$ modified in this manner. The quantity $\langle \mathbf{r}^{\mathrm{T}}\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0$ thus obtained is properly representative of just those configurations for which bond i is in state η, all other configurations being rejected.

Since

$$p_{\eta;i} = Z'_{(\eta;i)}/Z \quad (31)$$

we have by substitution of eq 30 into eq 10

$$\beta_{2;i} = (6/5Z)\mathcal{J}^*\mathbf{A}_1{}^{(i-1)}\boldsymbol{\epsilon}_i{}^{-1}\mathbf{B}_{\eta;i}'\mathbf{C}_{i+1}{}^{(n-i-1)}\mathcal{J}/p_{\eta;i}\langle r^2\rangle_0 \quad (32)$$

Methods for evaluating $p_{\eta;i}$ have been given previously.[4,8] The quantity $\langle r^2\rangle_0$ in eq 31 should represent exclusively those configurations in which bond i is in state η. However, the value of $\langle r^2\rangle_0$ usually will be only minutely affected by this restriction. Hence, we ignore it and use the value of $\langle r^2\rangle_0$ averaged over all configurations of the chain in equations and calculations that follow.

The mean correlation of the transition moments throughout the chain with the vector $\mathbf{r}$ may be obtained by methods previously used for treatment of strain birefringence. According to eq 14 and 32

$$G_2 = (6/5Z\langle r^2\rangle_0)\sum_i \mathcal{J}^*\mathbf{A}_1{}^{(i-1)}\mathbf{B}_{\eta;i}'\mathbf{C}_{i-1}{}^{(n-i-1)}\mathcal{J} \quad (33)$$

The sum on the right-hand side is given identically by

$$\mathcal{J}^*(\mathcal{Q}_{\eta;i}')_1{}^{(n)}\mathcal{J}$$

where[9]

$$\mathcal{Q}_{\eta;i}' = \begin{bmatrix}\mathbf{A} & \mathbf{B}_\eta'\\ \mathbf{O} & \mathbf{C}\end{bmatrix}_i \quad (34)$$

Hence

$$G_2 = (6/5Z\langle r^2\rangle_0)\mathcal{J}^*(\mathcal{Q}_\eta')_1{}^{(n)}\mathcal{J} \quad (35)$$

Cases in which ϵ_i is equal to ϵ_η for all active absorbing groups are the ones of main interest. It will be expedient in such cases to replace $\mathcal{Q}_{\eta;i}'$ by

$$\mathcal{R}_{\eta;i}' = \begin{bmatrix}\mathbf{A}_i & \epsilon_\eta{}^{-1}\mathbf{B}_{\eta;i}'\\ \mathbf{O} & \mathbf{C}_i\end{bmatrix} \quad (36)$$

Then (compare eq 16)

$$G_2 = (6\epsilon_\eta/5\langle r^2\rangle_0 Z)\mathcal{J}^*(\mathcal{R}_\eta')_1{}^{(n)}\mathcal{J} \quad (37)$$

The matrix $\epsilon_i{}^{-1}\mathbf{B}_{\eta;i}'$ differs from $\mathbf{B}_{\eta;i}'$ through replacement of $\hat{\boldsymbol{\epsilon}}_i$ (and its row and column forms, see eq 27) by $\hat{\boldsymbol{\epsilon}}_i/\epsilon_i = \hat{\boldsymbol{\epsilon}}_i/\epsilon_\eta$.

In the event that a pair of consecutive skeletal bonds, *e.g.*, bonds $i-1$ and i, is required to comply with a specified conformation in order for absorption to occur, appropriate adaptation of the foregoing treatment may be achieved through replacement of $\mathbf{B}_{\eta;i}'$ by $\mathbf{B}_{\zeta\eta;i}'$ where ζ and η denote the required states of bonds $i-1$ and i respectively. If the absorption is contingent upon occurrence of a conformation involving a longer sequence of bonds, the necessary modification is accomplished as follows. Let s be the number of consecutive skeletal bonds comprising the sequence that must be conformed in a specified manner. The absorption may be arbitrarily ascribed to any bond of the s bonds of the sequence, since their conformations are mutually fixed. Then let

$$\mathbf{B}_{i,s}' = \mathbf{B}_i'\mathbf{C}_{i+1}'\ldots\mathbf{C}_{i+s-1}' \quad (38)$$

The primes appended to each factor on the right-hand side will be understood to denote replacement of elements for inactive conformations by zero in the statistical weight matrix for the indexed bond. Similarly

$$\mathbf{U}_{i,s}' = \mathbf{U}_i'\ldots\mathbf{U}_{i+s-1}' \quad (39)$$

then

$$\langle \mathbf{r}^T\hat{\boldsymbol{\epsilon}}_i\mathbf{r}\rangle_0 = \frac{2\mathcal{J}^*\mathbf{A}_1{}^{(i-1)}\mathbf{B}_{i,s}'\mathbf{C}_{i+s}{}^{(n-i-s)}\mathcal{J}}{\mathbf{J}^*\mathbf{U}_1{}^{(i-1)}\mathbf{U}_{i,s}'\mathbf{U}_{i+s}{}^{(n-i-s)}\mathbf{J}} \quad (40)$$

where $\mathbf{J}^*$ is the row with elements 1,0,0 and $\mathbf{J}$ is the column with elements 1,1,1. $\beta_{2;i}$ and G_2 may be obtained from eq 40 by resort to the procedures set forth above.

The foregoing treatment is readily adapted to the case in which the transition moment $\mathbf{m}_i$ (and the associated tensor $\boldsymbol{\epsilon}_i$) for bond i assumes a magnitude and/or direction within the local reference frame (*e.g.*, the reference frame of bond i) that depends on the rotational state of that bond, and perhaps also on the state of its neighbor (predecessor). All that is required is the revision of $\mathbf{B}_i$

$$\mathbf{B}_i = \begin{bmatrix} \|\mathbf{U}_{\zeta\eta}\hat{\boldsymbol{\epsilon}}_{\zeta\eta}{}^{\mathrm{R}}\|\mathrm{diag}(\mathbf{T}_\eta \times \mathbf{T}_\eta) & \|\mathbf{U}_{\zeta\eta}\hat{\boldsymbol{\epsilon}}_{\zeta\eta}{}^{\mathrm{R}}(\mathbf{I}\times\mathbf{E}_3)\|\mathrm{diag}(\mathbf{T}_\eta) & (1/2)\|\mathbf{U}_{\zeta\eta}\hat{\boldsymbol{\epsilon}}_{\zeta\eta}{}^{\mathrm{R}}(\mathbf{I}\times\mathbf{I})\| \\ \mathbf{O} & \|\mathbf{U}_{\zeta\eta}\hat{\boldsymbol{\epsilon}}_{\zeta\eta}\|\mathrm{diag}(\mathbf{T}_\eta) & \|\mathbf{U}_{\zeta\eta}(\mathbf{E}_3\times\mathbf{I}^{\mathrm{T}})\hat{\boldsymbol{\epsilon}}_{\zeta\eta}{}^{\mathrm{C}}\| \\ \mathbf{O} & \mathbf{O} & \|\mathbf{U}_{\zeta\eta}\hat{\boldsymbol{\epsilon}}_{\zeta\eta}{}^{\mathrm{C}}\| \end{bmatrix}_i \quad (41)$$

which may then be used instead of $\mathbf{B}_i'$. Here $\|\ \|$ denotes matrix development of the element $\zeta\eta$ enclosed, and $\mathrm{diag}(\mathbf{T}_\eta)$ replaces $\|\mathbf{T}_\eta\|$, etc., in a previous notation.

(8) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, in press.

(9) The matrix defined according to eq 34 with $\mathbf{B}_{\eta;i}'$ replaced by $\mathbf{B}_i$ corresponds to the matrix $\mathcal{Q}_i$ introduced previously[3,4] for treating the strain birefringences, the traceless polarizability tensor $\bar{\boldsymbol{\alpha}}_i$ being replaced by $\hat{\boldsymbol{\epsilon}}_i$. In the interests of resolving $\mathcal{Q}_i$ into the submatrices as in eq 34, third and fourth pseudorows and third and fourth pseudocolumns of the previous $\mathcal{Q}$ have been interchanged.

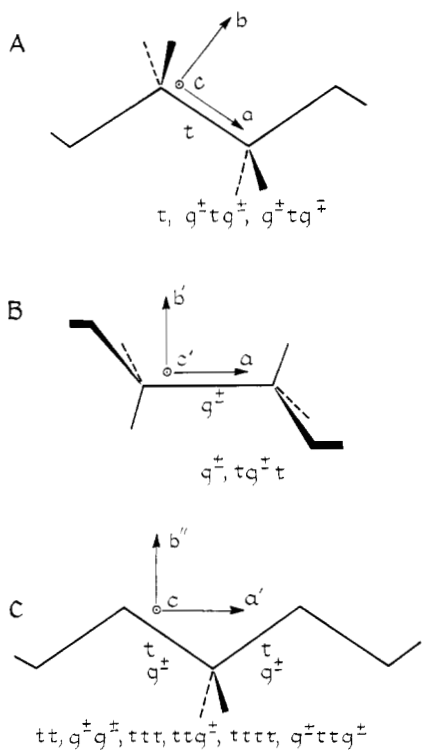

Figure 1. Orthogonal axes defined for the conformations indicated.

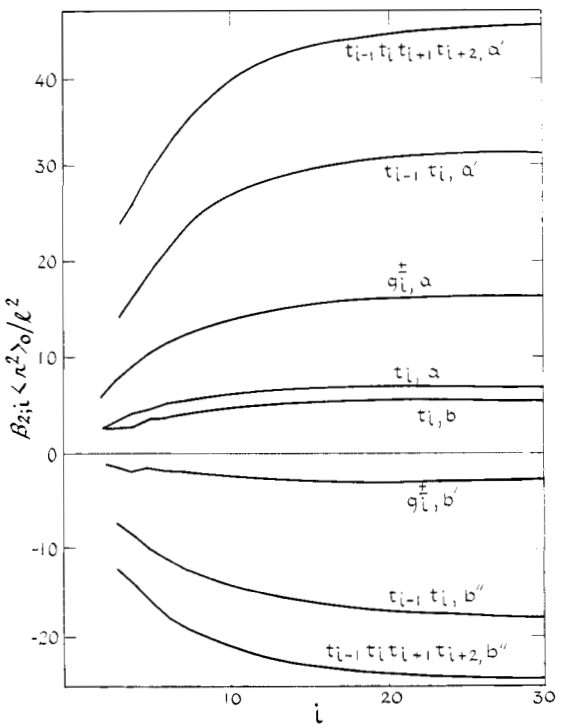

Figure 2. Values of $\beta_{2;i}\langle r^2\rangle_0/l^2$ calculated for a polymethylene chain plotted against i. Calculations were carried out with $\sigma = 0.544$, $\omega = 0.0875$, and $n = 515$.

Certain simplifications are possible if the end-to-end directions within the chain are indistinguishable, and if, further, the conformational group $i-1$, i, or i, $i+1 \ldots i+s-1$ is symmetric with respect to the same operation of end-to-end reversal. Then, terms in which $\mathbf{l}_j$, $\mathbf{l}_k$ and $\hat{\boldsymbol{\epsilon}}_i$ occur in the order $i < k, j$ are qual to corresponding terms with $k, j < i$. Deleting the former and doubling the latter, we replace 27 and 28 for $\mathbf{B}_i$ and $\mathbf{C}_i$ by

$$\mathbf{B}_i = \begin{bmatrix} \mathbf{0} & (1/2)\mathbf{U}[(\mathbf{l}^{\mathrm{T}} \times \mathbf{l}^{\mathrm{T}})\hat{\boldsymbol{\epsilon}}^{\mathrm{C}}] \\ (\mathbf{U} \times \hat{\boldsymbol{\epsilon}})_{\parallel}\mathbf{T}_{\parallel}^{\prime\prime} & 2\mathbf{U} \times [(\mathbf{E}_3 \times \mathbf{l}^{\mathrm{T}})\hat{\boldsymbol{\epsilon}}^{\mathrm{C}}] \\ \mathbf{0} & 2\mathbf{U} \times \hat{\boldsymbol{\epsilon}}^{\mathrm{C}} \end{bmatrix}_t \quad (42)$$

$$\mathbf{C}_i = \begin{bmatrix} (\mathbf{U} \times \mathbf{E}_3)_{\parallel}\mathbf{T}_{\parallel}^{\prime\prime} & \mathbf{U} \times \mathbf{l} \\ \mathbf{0} & \mathbf{U} \end{bmatrix}_t \quad (43)$$

The matrices $\mathcal{Q}_{\eta;i}'$ and $\mathcal{R}_{\eta;i}'$ are then obtained according to eq 34 and 36, respectively, by combining the condensed matrices given above (with deletions appropriate to the extinction $\boldsymbol{\epsilon}_{\eta;i}$) and matrix $\mathbf{A}_i$ given by eq 26, the latter matrix being unchanged. Use of $\mathbf{B}_i$ and $\mathbf{C}_i$ defined by eq 42 and 43 lowers the order of the matrices required for numerical calculations, which are simplified accordingly.

Results of Numerical Calculations

Orthogonal axes chosen to conform with symmetry features for various conformations are specified in Figure 1. In the case of a *trans* (t) bond, the appropriate set of axes, shown in Figure 1A, are an axis a taken along the C—C bond, an axis b in the plane of this bond and its adjoining skeletal bonds, and c perpendicular to that plane. If the bond in question is *gauche* ($g^{\pm}$), the axis a is again taken along the bond, but, as shown in Figure 1B, the second axis b' is taken in the plane which bisects the dihedral angle of rotation from the *trans* conformation; the axis c' is then the twofold axis. Figure 1C represents the case in which two consecutive bonds are in the same conformation, *i.e.*, tt, g^+g^+, or g^-g^-. Then the axis a' is located in the direction parallel to the sum of the two bond vectors (each taken left to right); b'' is assigned the direction specified by the difference between the two vectors, and c is normal to the plane defined by the two bonds. Triad conformations $g^{\pm}tg^{\pm}$ and $g^{\pm}tg^{\mp}$ are comprehended by Figure 1A, and triads $tg^{\pm}t$ by Figure 1B. The various triad and tetrad conformations listed below Figure 1C may be interpreted in terms of the axes specified therein.

The following structural parameters were adopted

$$l_{\mathrm{C-C}} = 1.53 \text{ Å}$$

$$\theta = \pi - \angle\mathrm{CCC} = 68°$$

$$\varphi_t = 0°; \quad \varphi_{g^{\pm}} = \pm 120°$$

The usual statistical weight matrix[4,10]

$$\mathbf{U} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \quad (44)$$

for a simple chain comprising identical bonds subject to threefold potentials was used. The parameters σ and ω are considered to be related to conformational energies according to

$$\sigma = \exp(-E_\sigma/RT) \quad (45)$$

$$\omega = \exp(-E_\omega/RT) \quad (46)$$

Calculations were carried out for selected numerical values of the parameters σ and ω chosen to simulate polymethylene chains at 140°. The values chosen

TABLE I
VALUES OF G_2^* CALCULATED FOR A POLYMETHYLENE CHAIN OF n = 515 BONDS, WITH σ = 0.544 AND ω = 0.161

Conformation	Axis						
	a	a'	b	b'	b''	c	c'
t	0.998		0.838			−1.836	
$g^{\pm}$	2.298			−0.331			−1.967
tt		4.566			−2.360	−2.206	
$g^{\pm}g^{\pm}$		1.016			−1.847	0.831	
ttt		5.468			−2.694	−2.774	
$ttg^{\pm}$		3.526			−1.973	−1.553	
$g^{\pm}tg^{\mp}$	−1.410		3.567			−2.157	
$g^{\pm}tg^{\mp}$	−2.326		2.650			−0.324	
$tg^{\pm}t$	4.489			−1.973			−2.515
$tttt$		6.606			−3.380	−3.226	
$g^{\mp}ttg^{\mp}$		2.345			−2.506	0.161	

TABLE II
VALUES OF G_2^* CALCULATED FOR A POLYMETHYLENE CHAIN OF n = 515 BONDS, WITH σ = 0.544 AND ω = 0.0875

Conformation	Axis						
	a	a'	b	b'	b''	c	c'
t	1.049		0.843			−1.892	
$g^{\pm}$	2.438			−0.337			−2.101
tt		4.700			−2.441	−2.259	
$g^{\pm}g^{\pm}$		1.118			−1.957	0.838	
ttt		5.588			−2.770	−2.819	
$ttg^{\pm}$		3.656			−2.054	−1.602	
$g^{\pm}tg^{\pm}$	−1.434		3.686			+2.252	
$gt^{\pm}g^{\mp}$	−2.393		2.728			−0.335	
$tg^{\pm}t$	4.578			−1.996			−2.582
$tttt$		6.708			−3.445	−3.263	
$g^{\mp}ttg^{\pm}$		2.452			−2.618	0.166	

TABLE III
VALUES OF G_2^* CALCULATED FOR A POLYMETHYLENE CHAIN OF n = 515 BONDS, WITH σ = 0.377 AND ω = 0.0875

Conformation	Axis						
	a	a'	b	b'	b''	c	c'
t	1.500		0.832			−2.332	
$g^{\pm}$	3.046			−0.701			−2.345
tt		5.387			−2.681	−2.706	
$g^{\mp}g^{\pm}$		1.291			−2.148	0.857	
ttt		6.264			−3.026	−3.238	
$ttg^{\pm}$		3.968			−2.120	−1.849	
$g^{\pm}tg^{\mp}$	−1.859		4.367			−2.509	
$g^{\pm}tg^{\mp}$	−2.845		3.381			−0.536	
$tg^{\pm}t$	4.973			−2.183			−2.790
$tttt$		7.326			−3.650	−3.676	
$g^{\pm}ttg^{\pm}$		2.549			−2.771	0.221	

(see Tables I–III) correspond at this temperature to conformational energies as follows: (E_σ, E_ω) = (500, 1500), (500, 2000), and (800, 2000), expressed in calories per mole. The second pair is believed to be most nearly representative of the polymethylene chain.[4,10]

The average correlation for a moment associated with the ith bond of a chain is appropriately represented (see ref 6) by $\langle r^2\rangle_0\beta_{2;i}/l^2 = (^3/_5)\langle \mathbf{r}^{\mathrm{T}}(\hat{\epsilon}_i/\epsilon_i)\mathbf{r}\rangle_0/l^2$. This quantity, calculated according to eq 30 with σ = 0.544 and ω = 0.0875, which values correspond to (E_σ,E_ω) = (500, 2000 cal mol^{-1}) at a temperature of 140°, is plotted in Figure 2 against i for the various conformations and the axes indicated. These calculations were carried out for chains of length n = 515 bonds. Increasing the length of the chain to n = 1027 bonds altered the results by less than 0.5%. Hence, the curves in Figure 2 may be considered to be representative of chains of unrestricted length.

Appreciable end effects[8] are evident in Figure 2. Close approach to asymptotic values obtains in all cases beyond i = 20, however. Only two axes are represented for each conformation; the correlation with the third follows from the condition

$$\beta_{2;i}{}^a + \beta_{2;i}{}^b + \beta_{2;i}{}^c = 0 \qquad (47)$$

which of course is a consequence of

(10) A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966).

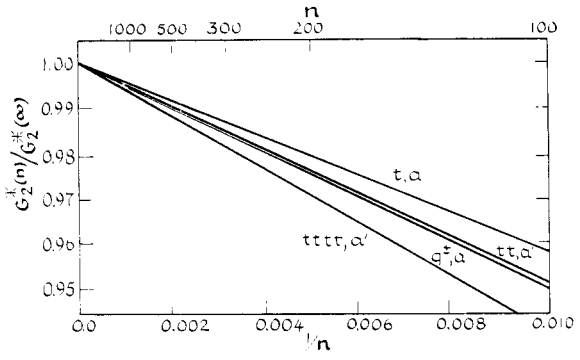

Figure 3. Ratios $G_2^*(n)/G_2^*(\infty)$ for various conformations and axes within polymethylene chains plotted against $1/n$. Calculations carried out for $\sigma = 0.544$ and $\omega = 0.0875$.

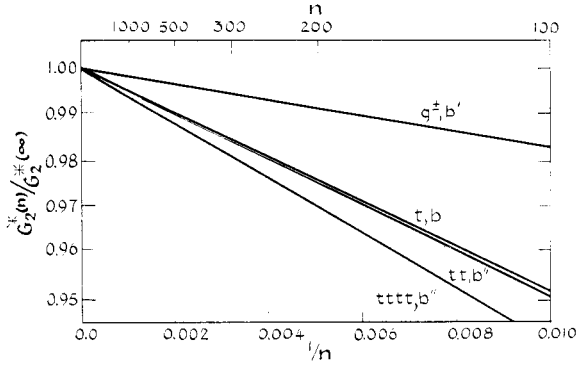

Figure 4. Continuation of Figure 3.

$$\cos^2 \Phi_i^a + \cos^2 \Phi_i^b + \cos^2 \Phi_i^c = 1$$

Correlations of axes with **r** for the various axes and conformations differ widely, as was to be expected. Before turning to comparisons of these results, we shall examine correlations averaged over all bonds i of the chain.

A proper measure of the mean susceptibility of an axis to orientation with respect to **r** is afforded by the quantity

$$G_2^* = G_2/\epsilon_\eta p_\eta \tag{48}$$

for the case in which the magnitude of the transition moment for each absorbing group is the same. Division by ϵ_η has the effect of replacing the transition moment by a unit vector. The quantity p_η is the mean expectation of the conformational state η required for absorption. Specifically

$$p_\eta = \sum_i p_{\eta;i}/n' \tag{49}$$

where n' is the number of bonds or bond sequences eligible to assume the state η (*i.e.*, n' is the number of terms in the sum over i). Methods for computing p_η have been given previously.[8] Division by p_η (see eq 48) adjusts the correlation with the vector **r** so that it reflects the effect per group in the active conformation. Recasting eq 24 in terms of G_2^*, we have

$$D - 1 \approx (3G_2^*/2n')(V/V_0)^{2/3}(\alpha^2 - 1/\alpha) \tag{50}$$

Values of G_2^* calculated according to eq 37 and 48 are presented in Tables I–III for the parameters σ and ω given in headings of the tables. The calculations were simplified through use of eq 42 and 43 in the construction of the matrices $\mathfrak{R}_{\eta;i}'$. The values of $\langle r^2\rangle_0$ required by eq 37 were computed by methods given previously.[4,10] Dependences of several of these quantities on n are shown in Figures 3 and 4, where $G_2^*(n)$, expressed as its ratio to its limit $G_2^*(\infty)$, is plotted against $1/n$. The limiting values were determined by extrapolation beyond the greatest chain length, $n = 515$, for which calculations were carried out. The plots are nearly linear over the range for $n > 100$; the difference $G_2^*(\infty) - G_2^*(515)$ amounts to only about 1%. The results given in Tables I–III may therefore be construed as limiting values with negligible error.

Comparison of results in the three tables shows the effect of decreasing E_ω from 2000 cal mol^{-1} (Table II) to 1500 cal mol^{-1} to be small. An increase of E_σ from 500 to 800 cal mol^{-1} has a greater effect, as was to be expected. However, the relative order of the orientational correlations is not substantially affected.

Discussion

According to the calculations reported in the first two rows of Tables I–III, a *gauche* bond is much more highly oriented with respect to the chain vector **r** than is a *trans* bond. Thus, for a *trans* bond with neighbors unspecified, the orientation of the b axis (see Figure 1A) with respect to **r** is almost as great as for its a axis, which is parallel to the C—C bond. For a *gauche* bond with neighbors unspecified, the a axis is strongly oriented preferentially, the axis b' assumes a small transverse orientation, and the c' axis exhibits a marked preference for transverse orientation. (The sum of the values of G_2^* along the three orthogonal axes vanishes, for reasons cited above.)

If the *trans* bond is situated between two *gauche* neighbors, its orientation (a axis) is transverse; the b axis, on the other hand, exhibits a pronounced orientation in the direction of vector **r**. Prescription of *trans* neighbors for a *gauche* bond enhances its parallel orientation, as comparison of the entries in Tables I–III for $tg^{\pm}t$ and for $g^{\pm}$ shows.

For conformations covered by Figure 1C, in which each of the central pair of bonds is assigned the same rotation, the a' axis, lying in the direction of the sum of the bond vectors, is oriented positively. This orientation is dominant in all such cases with the exception of $g^{\pm}g^{\mp}$ and $g^{\pm}ttg^{\pm}$, for which the preferential orientation of the b'' axis *transverse* to **r** is the most prominent feature. Lengthening the *trans* sequence from *tt* to *ttt* and to *tttt* increases the parallel orientation of the chain axis vector a', as would be expected.

The foregoing calculations may be compared with observations on infrared dichroism. The calculations refer, of course, to the range of small deformations where truncation of eq 6 is justified, whereas the experiments necessarily are conducted at the comparatively high strains required for measurable dichroism. The experiments of Read and Stein[1] were carried out on semicrystalline polyethylenes. Dichroic ratios D were determined for frequencies absorbed exclusively by the amorphous component; or, in the case of a frequency absorbed by both phases, the dichroic ratio D was estimated for the amorphous phase alone. The elongation within the amorphous regions may considerably exceed

the nominal (macroscopic) elongation α of the specimen, however.

Making comparisons at $\alpha = 2$, we note from the work of Read and Stein[1] that $D - 1 \approx 4.5$ for the 2016-cm^{-1} combination band representing *trans* sequences ... *tttt*... of more than four bonds. The transition moment is parallel to the a' axis (Figure 1C). Our calculations, with $\sigma = 0.544$ and $\omega = 0.0875$, give $G_2^*(a') = 6.7$ for the *tttt* conformation. The values of $D - 1$ and G_2^*(calculated) are not to be compared directly; they are significant only in relation to values for other bands.

For the 1352-cm^{-1} wagging frequency of the CH_2 group situated between *gauche* ($g^{\pm}g^{\pm}$) bonds, Read and Stein found $D - 1 \approx 0.3$ at $\alpha = 2$. Its transition moment is in the direction of axis a' (Figure 1C). Our calculations yield $G_2^*(a') = 1.1$.

The transition moment for the 1303-cm^{-1} band, representing wagging of the CH_2 groups in $g^{\pm}tg^{\pm}$ and $g^{\pm}tg^{\pm}$ conformations, is directed between the a and b axes of Figure 1A. According to Read and Stein, $D - 1 \approx 0.1$ at $\alpha = 2$. Our calculations, confined to symmetry axes taken individually, yield $G_2^*(a) = -1.4$ and -2.4 for the $g^{\pm}tg^{\mp}$ and $g^{\pm}tg^{\mp}$ conformations, respectively, and $G_2^*(b) = 3.7$ and 2.7 correspondingly for the b axis. Hence, the calculated results are consistent with a value of $D - 1$ near zero.

The 1078-cm^{-1} band is attributed[1,11] to C—C bond stretching for both t and g conformations. The transition dipole for the former is very small owing to the centrosymmetry of the bond in this conformation. Hence, this band may be assumed to arise preponderantly from *gauche* bonds. The transition moment is parallel to c' (Figure 1B). According to the results of Read and Stein,[1] $D - 1 = -0.3$ at $\alpha = 2$. We obtain $G_2^*(c') = -2.1$.

Qualitative agreement between the calculated preferential orientations and infrared dichroic measurements is demonstrated by these comparisons. It is noteworthy that the conventional model of a chain comprising freely jointed segments is incapable of interrelating dichroism and the location of the transition moment within the skeletal structure of the real chain.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force office of Scientific Research Contract No. F 44620-69-C-0058.

(11) R. G. Snyder, *J. Chem. Phys.*, **47**, 1316 (1967).

On the Statistical Thermodynamics of Spherical and Chain Molecule Fluids

Robert Simha[1a] **and Thomas Somcynsky**[1b]

Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received March 12, 1969*

ABSTRACT: An improvement of the cell model for the liquid state by the introduction of vacancies in the lattice is considered. Two alternative assumptions (I and II), relating the cell partition function to the equilibrium fraction of vacancies, are employed. In I we average linearly over "solidlike" and "gaslike" free lengths or modes of motion, and in II over the free volumes themselves. The square-well approximation to the cell potential is used and nonnearest neighbor contributions to the lattice energy are included. The theory is applied to both spherical and chain molecules. In the liquid state, the properties studied are the equation of state, the cohesive energy, the internal entropy, and the internal pressure. For spherical molecules, critical and vapor pressure data and isotherms in the dense gas region are also computed. The comparison with experimental data of argon makes use of the reducing factors derived from second virial coefficients. Formulation I is found to be considerably superior to both the cell model and assumption II. For polymers a superposition procedure must be used for purposes of comparison. In contrast to the cell theory, the hole theory, in either formulation, describes accurately the experimental reduced zero pressure isobar over the whole range. Although promising, no decisive superiority over the cell theory in respect to other properties is observed in the present formulation. The theory does not lead strictly to a principle of corresponding states, but the resulting families of curves are practically superimposable. In order to compare the relative position of theory and experiment for the two types of liquids, the analysis of argon data is repeated by means of a superposition procedure. Differences appear in respect to the internal pressure and the compressibility, suggesting that the basic steps used to make the transition from spherical to chain fluids must be reexamined.

I. Introduction

In recent years increasing attention has been given to finding general relations which describe thermodynamic properties of chain molecule liquids and amorphous polymers. In addition to the intrinsic problem in the theory of the liquid state, these relations are needed in order to estimate physical properties under conditions unavailable experimentally and as a tool in the study of mixtures. The transition from the theoretical approach for spherical molecules to the case of chain liquids was made possible by Prigogine's introduction[2a] of the concept of external degrees of freedom. Subsequently,

(1) (a) Division of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 41106. (b) Département de Chimie, Université de Sherbrooke, Sherbrooke, P. Q., Canada.

(2) (a) I. Prigogine, "The Molecular Theory of Solutions," North Holland Publishing Co., Amsterdam, 1957; (b) J. Hijmans, *Physica*, **27**, 433 (1961).